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Memoirs of the Department of Agriculture in India

SOIL GASES

STORAGE

BY

J. WALTER LEATHER, V.D., F.I.C.

Imperial Agricultural Chemist

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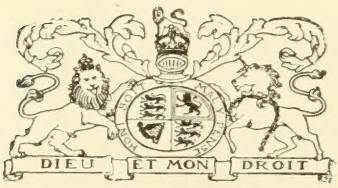

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SOIL GASES

BY

J. WALTER LEATHER, V.D., F.I.C.,

Imperial Agricultural Chemist.

Introduction.

Some years ago, after designing the soil-sampling tool which was described in Memoir, Vol. I, No. 6 of this series, I endeavoured to add an attachment by the aid of which the gases could be pumped out of the undisturbed soil enclosed in the cylinder. Hitherto samples of the gases contained in soils have been obtained by investigators by aspirating through a tube which had been inserted into the soil, and it is evident that under such circumstances contamination with common air would be probable ; in any case the precise source (*i.e.*, depth) from which such gas specimens are derived would be uncertain, and the estimation of the volume of gas per unit volume of soil would not be possible. If, however, the gases included in the small cylinder of undisturbed soil, which my boring tool withdraws from the land, could be separated, its volume could be compared with that of the soil, the exact position with reference to depth would be known, and contamination with outside air would be excluded.

It was, however, not an easy matter to devise a suitable attachment, and although one was made several years ago, experience with it showed that it included certain defects. It was only about a year ago that the difficulties were finally overcome, and the apparatus, which is described in the first section of this memoir, designed and made.

Having succeeded in this, the apparatus was employed to obtain more definite information than we possess in relation to specific agricultural conditions such as, the gases present during the decomposition of green manure, the gases of swamp rice soil, the assimilation of nitrogen by *Papilionaceæ*, the gases present near the roots of crops, changes during nitrification.

Another question readily presented itself, namely, would it be possible to determine in a given case whether oxygen or nitrogen had been set free or

combined ? It is evident that the mere analysis of the gases would not answer this question, for although in the event of finding a large increase in the amount of carbon dioxide and an approximately corresponding decrease of oxygen, the conclusion would be admissible that the oxygen had been simply utilized in an oxidation process, still this is a mere assumption, and in other possible cases the percentage composition would only show changed proportions of oxygen and nitrogen, but would not admit of a conclusion as to whether the one gas had been liberated or the other assimilated. There was one possible means of solving such a question, namely, the estimation of the argon. Since argon takes no part in animal or plant economy,[1] its ratio to the oxygen or nitrogen in soil gases would show definitely whether there is in the soil a higher or a lower ratio than in the atmosphere, and thereby provide an answer to the foregoing question. Considerable time was therefore spent in devising the most suitable means of estimating this element with sufficient precision for the purpose, when operating with comparatively small amounts of gas. The amount of argon has not, I believe, been estimated hitherto in such small volumes of gas as are referred to in this contribution. It seems therefore desirable to set out a number of the details of manipulation which I have found useful in order to reduce as far as possible the error in its determination.

Having obtained information regarding the composition of soil gases under these various conditions, attention was directed to the rate of diffusion of gases out of and into the soil in order to form an estimate of the quantities involved, and this forms the subject of the later paragraphs.

I wish to take this opportunity of expressing my obligations to my friend, Mr. W. H. Harrison, Agricultural Chemist to the Government of Madras, for kindly supplying me with samples of the gases of swamp rice lands (a subject which he has had under investigation[2] for several years), in order that I might determine the proportion of argon in them ; also to Dr. F. P. Harrison, of the Indian Educational Service, for kindly criticism of the paragraphs regarding diffusion.

Since writing the manuscript of this memoir, the contribution on soil gases by Russell and Appleyard[3] has appeared. The methods employed,

[1] MacDonald & Kellas, *Proc. Roy. Soc.*, 1895, **57**, 490.

[2] *Mem. Dept. Agri. Ind., Chem. Series,* Vol. III, No. 3, and Vol. IV, No. 1.

[3] E. J. Russell & A. Appleyard, The atmosphere of the soil ; its composition and the causes of variation. *Jour. Agric. Sci.* (1915), VII, 1.

as also the objects in view at Pusa and at Rothamsted respectively, have been so different that in a great measure the information provided is hardly comparable. But one or two points seem to be definite ; (i) the soil in India generally or often contains much more carbon dioxide than soil in England, (ii) in both countries a considerably larger amount of oxygen passes into combination within the soil than is accounted for by the carbon dioxide produced.

Russell and Appleyard employ the term " soil atmosphere " or " soil air " to represent what is actually the gaseous phase in the soil. In my view it is a mistake to employ the term " atmosphere " or " air " in this case. It is true that one speaks of the " atmosphere " of mines, of caves, or of underground chambers, but in each of these cases the gas mixture is either suitable for humans or is artificially made so, whereas the gaseous mixture in the soil is often (at least in India) so different that a humanbeing could not exist in it, whilst plants flourish. It is moreover a gaseous mixture which is constantly suffering changes in part by chemical or biological agency, in part according as there is much or little water present.

Another recent contribution bears indirectly on the subject of soil gases in their relation to plant life. Messrs. Briggs & Shantz,[1] when determining the amount of water transpired by farm crops, grew the plants in jars of earth which were entirely sealed over with wax, that is, these plants grew to maturity under conditions approaching " no aeration." This evidence is entirely at variance with popular ideas regarding soil gases and illustrates how little is known at present regarding the subject.

Apparatus and methods employed.

Apparatus for the abstraction of soil gases.—As has been briefly mentioned, the newly designed apparatus for the abstraction of soil gases consists of a suitable attachment to my soil-boring cylinder. A section of the iron cylinder is shown at A in fig. 1. In order to obtain the soil specimen, this cylinder, attached to a shaft, is forced into the ground, aided by a rotating motion, and after sinking to the required distance, withdrawn. The soil comes out of the bore-hole intact, both upper and lower faces being smooth or approximately so. The problem was to devise a means of enclosing this soil specimen in such a manner that the contained gases could be pumped out.

[1] Briggs & Shantz, Relative water requirement of Plants, *J. Ag. Research*, III, p. 1 to 63.

Among the several means which were tried with this end in view, one may be mentioned because it was employed for some time. The *upper* soil-surface in the cylinder was sealed by pouring molten Wood's alloy (m.p. about 80°C.) on to it. This seal was not perfectly tight after solidifying, but was made so by the addition of a layer of molten paraffin wax. The lower soil-surface was closed by passing a rubber cap over that end of the cylinder. The rubber cap was provided with a tube to which a glass tube and stop-cock could be attached. This method included two defects. Firstly, there was a difficulty in obtaining rubber caps to fit the cylinders sufficiently well; they could not be made in India and those obtained from Europe were frequently faulty. Secondly, although the temperature of the Wood's alloy was not very great, still the temperature of the soil was found to rise so seriously that improvement in this respect was desirable. Eventually the stopper and cap which are illustrated in fig. 1 were designed. The cap C which seals the lower soil-surface, is of iron and its side is ground to fit the lower end of the cylinder A. It is provided with a small outlet tube of about 1 mm. bore. If this cap is dipped into molten paraffin and then pushed on to the cylinder, the edges are quite gastight. The screw-plug S.P. which seals the upper soil-surface, consists of a rubber disk R which is compressed between the iron discs D′, D″, by means of the winged-nut W working on the screw. If this stopper with the screw relaxed, is placed inside the cylinder and then screwed tight, it also makes a perfect joint. When taking a soil specimen for gas analysis, the following procedure is adopted. A small flat dish of paraffin is heated. The cylinder is then forced into the soil at the required depth. Should this not be the surface soil, the soil above that which is required is first removed by other cylinders. Immediately on withdrawing the desired portion, the rubber stopper is placed, temporarily loose, in the cylinder; the lower cap is momentarily placed, inverted, in the molten paraffin so as to coat the edges only, and then pushed on to the cylinder; the soil is now substantially enclosed. The stopper is now screwed tight. To do this a T shaped box-wrench is placed on the upper end of the screw and turned against the winged-nut W, by which means the stopper is made gastight. In order to seal the edge of the lower cap more effectively, molten paraffin is applied to the edge by means of a brush. Finally in order to close the capillary outlet tube a rubber cap is passed over it. The whole procedure occupies a few seconds, and the two soil-surfaces are exposed to the air only momentarily. The cylinder or cylinders are then removed to the laboratory.

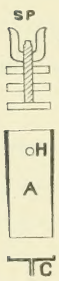

FIG. 1

In order to remove the gases, the apparatus which is illustrated in fig. 2 has been employed. To the cap of the soil cylinder is attached a capillary tube with tap T, and it is suspended in the glass jar J. The capillary tube is attached in turn to the flask F which stands in the glass jar K, and F is in turn attached to a Töpler pump. Flask F contains a small amount of mercury M to prevent it floating. Jar J is filled with cold water so as to submerge the cylinder A; jar K is filled with ice-cold water. All the several rubber connections are thus sealed under water. The object of using ice-cold water in jar K is to prevent water accumulating in the pump. So soon as the connections are made (tap T being closed) the apparatus is exhausted as far as tap T. Subsequently T is opened and the soil gases flow into the pump section, and may be collected at the pump outlet in a suitable gas-holder. The moisture in soils, more particularly when they are wet, offers a certain amount of resistance to the flow of a proportion of the gases, and on this account after most of the gas has been removed and the vacuum has become fairly good, warm water is added to jar J in order to raise its temperature to about 45°C. This naturally occasions the expulsion of the greater part of the water in the soil, and it is principally on this account that the cooled flask F is so useful. By the aid of the cold water in K most of the water vapour in the gas becomes condensed, and, since the temperature of the gas rises as it flows into the pump, condensation of moisture in the pump is avoided.

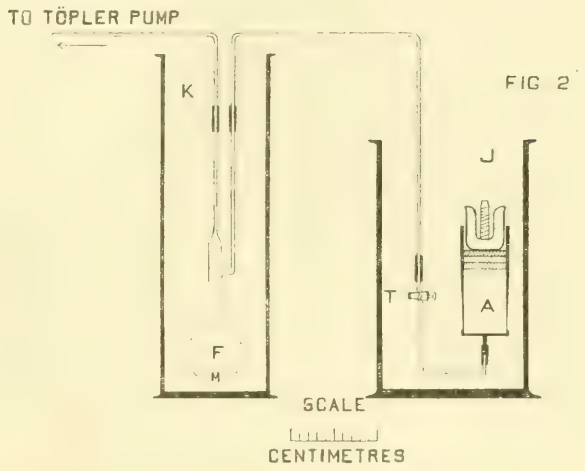

FIG 2

This apparatus has been found to fulfil its function very well; it is expeditious and has offered no inconveniences. The time required to separate the gases from a portion of soil usually occupies from $1\frac{1}{2}$ to 2 hours.

Estimation of hydrogen and hydrocarbons.—After removal of the carbon dioxide and oxygen, any hydrogen or hydrocarbon present must be determined, for these are not infrequently present in soil gases. To this end I have passed the gas over hot copper oxide as being more suitable than combustion in oxygen when the percentage of these gases is quite small.

It is perhaps well to refer here to the errors accompanying an operation such as the determination of small amounts of hydrogen. In Table X small percentages of hydrogen gas are stated to have been found in the neighbourhood of plant roots, and moreover this gas was not always found. For example, hydrogen (1·39%, 1·37%) was found near the roots of maize on the 6th and 8th September and none on 10th September, and the question naturally arises how far experimental error may be answerable either for the detection of the gas, or for its total absence. If hydrogen was being formed on the earlier dates, it is improbable that the process was entirely suspended on the later date. In some cases the same gas was passed over hot copper oxide a second time, and here we have the two measurements of the gas which should be equal; any difference is due to error. Again in other cases no hydrogen was found and any difference between the gas volume before and after the operation is due to error.

The probable error deduced from such measurements = ±0·045 c.c. the total volume of gas being about 50 to 60 c.c.; the probability is 25 : 1 that any difference after passage over copper oxide greater than 0·15 c.c. is a real difference.

Thus:

Samples of gas from neighbourhood of maize roots.

(i) Volume of gas after removing CO_2 & O .. 53·14 c.c.
Do. after passing over CuO .. 52·22 ,,

Δ = — 0·92 ,,

Do. after again passing over CuO .. 52·23 ,,

0·92 is a real difference due to hydrogen.

(ii) Volume of gas after removing CO_2 & O .. 42·16 ,,
Do. after passing over CuO .. 42·07 ,,

Δ = — 0·09 ,,

0·09 is possibly due to experimental error, but as the gas was one of a series in which hydrogen was usually present, the pre-

sumption is that this gas was actually present here.

(iii) Volume of gas after removing CO_2 & O	..	54·02	c.c.
Do. after passing over CuO	..	54·07	..
Δ =	+	0·05	,,

Here the difference is obviously due to experimental error.

Sample of gas from green-manured land.

(iv) Volume of gas after removing CO_2 & O	..	63·76	,,
Do. after passing over CuO	..	63·60	,,
Δ =	—	0·16	..

This difference is so much greater than the probable error that the probability is 25 : 1 that hydrogen was present.

The estimation of argon.—The correct estimation of argon offers no difficulties provided the volume of gas employed is considerable, but since I have not found in the literature any example of the determination of argon in small quantities of gas, such as are obtainable from soil by my apparatus, it will be of interest to others who may be engaged on the examination of soil gases, if the apparatus and *modus operandi* which I have employed are described in some detail.

The burette.—The gas-burette consisted in the upper part of a tube of about 4 mm. internal diameter by about 30 cm. long ; this was marked at each centimetre. 1 cm. = 0·15 c.c. approximately. The lower part of the burette consisted of a series of bulbs of approximately 3, 6, 12, 24 and 48 c.c. respectively, and the total volume was about 100 c.c.

Absorption of the nitrogen.—With considerable quantities of gas, the apparatus which was employed by Rayleigh and Ramsay[1] for the separation of argon from air or that used by Schloesing,[2] possesses the great advantage of causing the gas to pass repeatedly over the absorbent. But when working with the small amount of gas that was obtainable from small soil specimens,

[1] *Phil. Trans.*, 1895, Vol. 186, part 1, p. 212.
[2] *Compt. rend.*, 1895, **121**, 525.

this apparatus proved unpractical. After trial of several different arrangements, that which is illustrated in fig. 3 proved to be the best. Little expla-

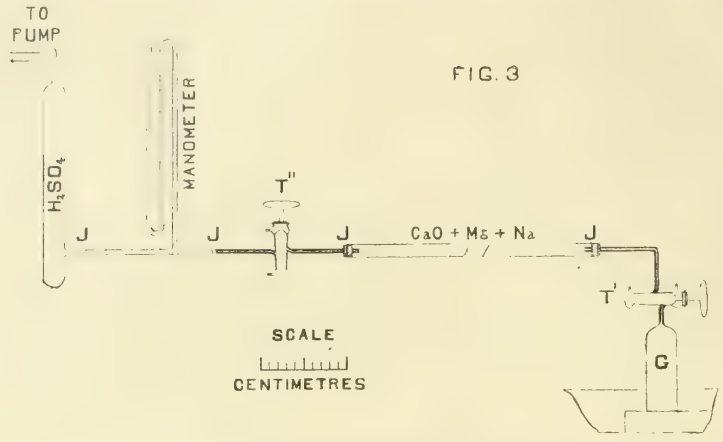

FIG. 3

nation is required. A mixture of good calcium oxide, magnesium and sodium is placed in the tube and kept in position by asbestos plugs. G is a small gas-holder full of mercury. Both taps T′. T″, as likewise all rubber junctions J, J, are mercury sealed. The tube marked H_2SO_4 contains pumice saturated with sulphuric acid. When carrying out an absorption, the air is first removed from the apparatus as far as tap T′. The lime-magnesium-sodium mixture is now heated to dull redness by a small furnace (not shown) and most of the hydrogen which is evolved is removed. Tap T″ is now closed. The residual gas, nitrogen and argon, is passed into the gas-holder G, and allowed to flow into the absorption tube. The nitrogen is absorbed very rapidly at a dull red heat, but since the first portion of the gas flows very quickly over the heated lime-magnesium-sodium, it is desirable to pass the gas over the absorbent repeatedly. To this end T″ is momentarily opened and then closed again. This allows a part of the residual gas to flow into the pump section. It is pumped out into a small tube and returned to the gas-holder G, whence it is allowed to re-enter the absorbing tube. After repeating this operation four or five times, the residual argon *plus* hydrogen is pumped out, and the hydrogen is subsequently removed by passing the gas over hot copper oxide.

The perfection of the absorption of the nitrogen, and thereby the accuracy of the argon determination, will be considered presently. There are, however, a number of details of manipulation which have been found to be necessary or desirable, and these may be here suitably considered.

(*a*) *The lime* has been obtained by heating good marble, broken to fragments of about 2 to 3 mm. diameter and containing not more than about 2 to 3% of carbonate.

(*b*) *The magnesium* has been in the form of a powder. It contains a small amount of hydrogen, but the mixture of magnesium, sodium and lime yields a much larger amount. This is apparently due to the action of the sodium on the lime, which almost necessarily contains a small amount of hydroxide, and to the presence of moisture in the magnesium powder. For example :—

		c.c.
(*i*)	Hydrogen obtained from 1 grm. magnesium ..	2·01
(*ii*)	Do. from 5 grm. lime *plus* sodium ..	32·72
(*iii*)	Do. from 5 grm. lime, 1 grm. magnesium and sodium	56·88

A small amount of carbon dioxide (about 3 c.c.) was evolved from the lime at the same time. The hydrogen commences to be liberated at a low temperature and the greater part is rapidly evolved, but the last portion of the mixture of CO_2+H is not readily removed in any reasonably short time. By keeping the pump in action for $\frac{1}{2}$–1 hour while the tube is at a dull red heat, the pressure is reduced to between 1 and 2 mm. and any hydrogen or carbon dioxide then remaining is of no consequence.

(*c*) *The mixture* employed is that recommended by Hempel, namely, 5 grm. calcium oxide, 1 grm. magnesium and 0·25 grm. sodium. The two former are weighed roughly and a suitable piece of sodium is measured by the eye, but cut clean under petrol. The two first named constituents are mixed rapidly in a tube : about one-half is introduced into the combustion tube, then the sodium (wiped free from petrol) is introduced, and finally the remainder of the lime-magnesium. A second asbestos plug is inserted, the tube fitted into its place in the apparatus and the air removed. These operations are performed as rapidly as possible, because it is of more importance to avoid unnecessary contact with the air, than to secure precise proportions of the ingredients. Hempel states that the quantities mentioned will absorb 326 c.c. of nitrogen, and the mixture certainly absorbs one-fourth of this quantity very perfectly.

(*d*) Before commencing to fill the combustion tube it is necessary that the gas-holder G shall be full of clean mercury up to and including tap T′. it is also desirable to have the pump-section from T″ exhausted, because in this case, most of the air of the combustion tube can be removed immediately after connecting it, by opening tap T″.

(*e*) *The combustion tube.*—For some of the earlier work quartz tubes were employed, but they possessed no real advantage over glass combustion tubing. They require careful cleaning, and are in any case attacked and gradually destroyed; also they are not all gastight. Good glass combustion tubing has proved more suitable and is generally quite gastight.

(*f*) *The junctions J.*—All taps and rubber connections are necessarily mercury sealed. For those marked J in fig. 3, pieces of glass tube with a hole cut in the side (see H. fig. 4) have proved the most serviceable. This hole is cut by holding the tube against a grind-stone until a sufficiently large oval-shaped aperture has formed for the introduction of mercury. The ends of this tube are joined to the tubes of the apparatus by corks. A ring of plasticine round the hole H forms a useful collar.

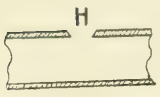

FIG. 4

(*g*) After absorption of the nitrogen, the following procedure has been followed for the removal of the argon. Tap T″ is momentarily opened and then closed. One "stroke" of the Töpler pump is then made. Tap T″ is then again opened and closed, followed by the removal of the gas in the pump. This operation is repeated eight or ten times. Finally, with tap T″ closed the whole of the remaining gas in the pump section is removed. The reason for this mode of operating is this. On opening tap T″ most of the gas (A + H) in the combustion tube passes into the pump section, and consequent on the reduction of pressure, more hydrogen is evolved from the magnesium. If then tap T″ remained open, the effect of pumping would be to cause a stream of hydrogen to pass out of the tube, and the argon from the further end of the tube would only pass out more or less by diffusion, unless the pump were kept in action until every trace of hydrogen had also been abstracted, which would certainly be a tedious process. But by closing tap T″ temporarily while the Töpler pump is actuated once, the hydrogen coming from the magnesium *displaces* the argon in part and on again opening tap T″ a proportion of the mixed gases passes out. Supposing the relative volumes of the Töpler pump and the combustion tube are (say) 3 : 1; then each time tap T″ is opened three-fourths of the gas in the combustion tube is removed, leaving only one-fourth; that is, by the procedure above outlined, only a small proportion of the argon remains in the combustion tube after each stroke of the pump. In case of the above proportions, one-fourth of the argon remains after the first stroke, one-sixteenth after the second, etc. If then the operation be repeated eight or ten times substantially all the argon is removed, without

troubling about the perfect removal of all the hydrogen. The total volume of A + H which has usually been collected in these operations has been some 5 to 10 c.c. most of which is hydrogen.

(*h*) The time occupied for the removal of the hydrogen from the magnesium mixture and the subsequent operations for the absorption of the nitrogen, and final removal of the residual hydrogen is about $2\frac{1}{2}$ hours.

(*i*) For the removal of the hydrogen and any carbon monoxide or dioxide from the argon, the gas is passed into a tube containing hot copper oxide, and at the cool end a small amount of soda-lime ; both being retained in position by asbestos plugs. The gas is circulated through this tube in the same manner as when absorbing nitrogen. Finally tap T″ is opened and all gas pumped out, which should now be pure argon. For this operation a quartz tube was found very suitable and proved quite gastight for many operations. Later, however, this tube came under suspicion of being slightly porous. The quantity of this air was very minute, but it seemed to be a definite leakage and the tube had in consequence to be laid aside. This is mentioned merely as an instance of a quartz tube being quite gastight for some months, and then becoming imperfect, without having anything in the nature of a crack.

The accuracy of the determination of argon.—In the following Table I are set out the results of determinations of argon in air. Here as in all other analyses detailed in this memoir unless specially mentioned, the volumes of gases are calculated at NT and P in the dry state :–

TABLE I.

Percentage of argon found in air.

Volume of air employed c.c.	Argon %	Ratio $\frac{N}{A}$
67·50	1·058	73·5
43·72	1·051	74·2
28·41	0·930	84·0
125·08	0·961	81·4
49·83	1·043	75·0
64·87	1·011	77·3
122·87	0·936	84·0
41·26	0·920	85·0
67·48	0·942	83·0
26·71	0·929	83·0

T. Schloesing[1] found, in a series of analyses of air in the neighbourhood of Paris, in which he employed about 1·5 litres of air for each analysis, from 0·9325 to 0·9369%A. In another series of samples of air taken at various places and elevations 1·192 volume of argon was found per 100 volumes of N+A, which is equivalent to 0·9425%A on the assumption of a normal percentage of nitrogen in the air. Kellas[2] found almost identical amounts.

It is evident therefore that about one-half of the percentages of argon found by my analyses are too high, a circumstance which is doubtless due to small amounts of nitrogen having escaped absorption by the CaO+Mg+Na mixture. None is too low. Considering the small amounts of gas employed the determinations are probably as accurate as one can expect.

The $\frac{N}{A}$ ratio derived from Schloesing's data is 83·2.

Proportions (by volume) of water and gases in the soil.

It will be evident that not only can the gases of a known volume of soil be extracted, but that also from the weight of fresh soil taken in the cylinder and, subsequently, the weight and sp. gr. of the dry soil material, the volumes of the three constituents—soil-material, water and gas—can be separately deduced. When making the calculations, that part of the carbon dioxide which is present in solution (see p. 100, of this memoir) must be deducted. The following examples may be suitably quoted :—

Soil depth.	2′ 6″—2′ 9″	3″—6″	12″—15″
	grm.	grm.	grm.
(*a*) Cylinder, etc., *plus* damp soil	1082·2	1060·7	1068·0
Cylinder, etc. ..	852·5	852·4	840·2
Damp soil *plus* wax ..	229·7	208·3	227·8
Wax	0·8	1·3	1·1
Damp soil.. ..	228·9	207·0	226·7
Dry soil	207·7	193·8	209·8
Water	21·2	13·2	16·9
	c.c.	c.c.	c.c.
(*b*) Soil material D = 2·71	76·64	71·51	77·42
Water ..	21·2	13·20	16·9
Gas at soil temp. and moist	59·38	68·79	61·62
	157·22	153·50	155·94
Volume of fresh soil ..	154·4	154·4	154·4

[1] *Comp. rend.* 1895 **121**, 601 and 1896, **123**, 696. [2] *Proc. Roy. Soc.* 1895, **59**, 66.

Condensed gas.—The difference between the sum of the estimated constituents and the volume of fresh soil is only small; usually the former is greater by 0·5 to 2·0 c.c. and indicates a small condensation of gas on the soil particles, but this fact is not very well established because an error of 1/32 inch in measuring the length of the soil column is equal to rather more than 2 c.c. in my apparatus. The volume of such condensed gas in the Pusa soil is certainly less than 4 % of the total gas present.

Gas compressed by surface tension.—One factor, which may in places operate on the volume of gases in soils is surface tension. Suppose a bubble of gas to be surrounded by water in some small cavity in the soil, the circumstances being that the quantity of water is so large that it is free to enter or leave the cavity. Under such circumstances the tension of the water—gas surface would tend to increase the pressure on the gas beyond that generally existing in the soil and which is approximately that of the atmosphere. This subject has not I think been referred to by others when discussing the physical properties of soils, and although no direct experimental data can be offered here, the matter is deserving of consideration, because quite small spheres would be exposed to considerable excess of pressure, and the corresponding decreased volume would be included in the difference between the volume of gas estimated and found, and would not be differentiated from gas condensed on the surface of soil particles in the foregoing method of measurement.

Although it is not possible to state the conditions with any great precision, the following limitation seems to be reasonable. In order that the water in any particular cavity may be free to exert its surface tension, its quantity must be considerable. It would not be sufficient for the cavity to be merely lined with water, with water-films closing its various mouths, because in such circumstances the surface tension would be as frequently negative as positive with respect to the enclosed gas. Considering various shaped cavities it seems doubtful whether the enclosed gas would possess the spherical shape and be surrounded by water sufficiently free to exert the full force of the surface tension unless the volume of water were at least twice that of the gas. Considering the relative volumes of water to gas in the Pusa soil generally, such a high proportion of water only occurs during the wettest weather and then only for a comparatively short time. Usually it may be said that, in this soil at least, the proportion of water to gas is so low that no large part of the gas could be present in the form of spheres surrounded by water sufficiently free to exert the pressure which we are now considering. Generally over the greater part of the year the major part of the gas must be free from this influence.

But here and there in the soil at any time, and more generally during the monsoon a part of the gas will be present as small spheres, and the increased pressure to which such gas would be subject is of interest. The pressure is represented by the equation :

$$p = \frac{2\,T}{r}$$

in which

p = pressure
T = surface tension
r = radius of sphere

It is evident that for very small spheres the pressure becomes considerable.

In the absence of direct measurements, the size of soil cavities is unknown, but they cannot generally have a smaller diameter than the average diameter of the soil particles, and probably such cavities are generally larger than this. The average diameter of the greater part of the Pusa soil particles varies from 0·0008 to 0·0032 cm. If it be assumed that the corresponding cavities include about half their volume of gas in the form of a sphere, the radius would lie between (about) 0·0003 and 0·0012 mm.

For temperature = 30°C, T = 71 dynes, and the increased pressure to which such spheres as those indicated would be subjected, lies between 470,000 and 120,000 dynes, or say between one-half and one-tenth atmosphere.

Volumes of water and gas.—A number of measurements of the soil constituents at different depths and at different seasons have been made, and Table II includes some examples. Regarding the volume occupied by the soil material this is usually in the neighbourhood of 50% and varies from 45 to 55% of the total. As this is comparatively constant whilst the proportions of water and gas vary within wide limits, only the latter are set out in the Table. It will be seen that the data contained in the first two columns refer to the state of the soil after long periods of practically dry weather. Then in June the effect of the monsoon rainfall becomes evident. The first rain is absorbed by the upper soil and the third column contains an example showing how so heavy a fall as 5·5″ in one week has not altered the proportion of water and gases materially in the third foot. In the same month, after a further fall of 5·3″ of rain in two weeks, the water has descended into the fourth foot. Later, during the same monsoon, the proportion of water increased somewhat and that of gases was reduced. The effect of continuous heavy rains for two months, was to reduce the percentage volume of gases from 35 or 40% in the hot weather to between 25 and 30% in the middle of July.

Table II.

Proportions (by volume) of water and gases in the soil.

Depth	1907 May 23rd to 27th.		1911 May 23rd to June 2nd.		1911 June 8th to 15th.		1911 June 27th to 29th.		1911 July 12th to 15th.		1911 July 18th to 20th.		1907 December 21st to 24th.		1908 January 3rd to 7th.		1908 January 8th to 11th.	
	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %	Water %	Gas %
0″—3″ ...	...	...	...	..	...	...	..	...	...	...	...	...	...	...	...	...	...	...
3″—6″ ..	12·0	35·6	6·0	41·2	...	...	..	...	..	...	...	...	.	..	...	...	...	..
6″—9″ ...	...	...	...		...	..	...		.	...	33·2	18·6	...	...	...	...	...	...
9″—12″ ...	...	...	..	...	...	...	27·1	23·6	...	...	28·2	26·6	21·5	26·4	24·8	20·0	18·2	30·8
1′ 0″—1′ 3″ ..	...	...	11·0	35 1	...	...	...	..	29·1	14·8	29·2	20·6	..	..	...	...	...	...
1′ 3″—1′ 6″ ...	...	...	...	..	...	...	...	..	...	...	...	...	...	...	.	...	...	...
1′ 6″—1′ 9″	...	...	...	...	...	...	..	...	...	...	...	...	.	...	...	.	...	...
1′ 9″—2′ 0″ .	16·4	30·3	...	...	...	...	20·3	31·9	...	...	...	...	28·2	17·1	25·7	25·4	13·4	39·0
2′ 0″—2′ 3″ ...	...	...	.	...	6·0	42·2	...	...	18·5	29·8	24·8	23·8	...	...	...	...	...	..
2′ 3″—2′ 6″	...	...	...	...	...	...	...	...	..	...	...	...	...	...	...	...	...	...
2′ 6″—2′ 9″ ...		...	...	...	...	...	...	...	...	...	...	...	...	...	..	...	..	...
2′ 9″—3′ 0″ ...	...	...	..	...	..	...	19·5	31·3	...	...	..	...	25·6	23·8	24·0	26·3	22·9	28·0
3′ 0″—3′ 3″ ...	6·9	45·3	4·2	42·2	8·3	42·3	.	...	27·4	21·2	26·4	21·7	..	...	...	...	...	...
3′ 3″—3′ 6″ ..	..	...	...	...	...	...	.	.		...	—	.	...	...	...	..	..	—
3′ 6″—3′ 9″ ...	...	...	..	...	...	...	...	...	...	...	...	...	...	.	...	...	...	—
3′ 9″—4′ 0″ ..	...		..	...	...	...	...		...	...			...	...	...	...	...	...
4′ 0″—4′ 3″ .	...			...	22·0	27·8	...	...	14·5	28·2	21·9	27·7	...		...	...	...	...
4′ 3″—4′ 6″	...	...	...	.	...	..	..		...	...	...	..	35·3	9·7	36·1	7·4	37·6	3·8
4′ 6″—4′ 9″ ..	...	...	...	..	...	...	...	...	...	...	...	..	..	.	...	...	..	...
4′ 9″—5′ 0″ ...	—		..	..	...	...	...	...		...	.	...	...	...	...	...	...	...
5′ 0″—5′ 3″ ...	24·4	22·7	20·2	2 2·6	19·2	25·3	...	..	...	...		...	...	...	...	...	...	...
Notes of rainfalls.	Feb. 5th to 7th 1·1″; March 11th to 12th 0·6″; March 16th to 18th 1·0″; otherwise no rain fell during the preceding 7 months.		January 27th 0·25″; March 2nd 0·33″; April 21st 0·34″. Total rain after Novr. 1st to date of sampling was 1·42″.		5·5″ of rain in one week which had been absorbed by the upper 2 ft. of soil and had not affected the 3rd foot.		After 5·3″ of rain in two weeks.		After 5·5″ of rain in two weeks.		After 3·5″ of rain in four weeks.		Monsoon rainfall ceased Sept. 24th after which there was no rain.		No rain subsequent to Sept 24th.		No rain subsequent to Sept. 24th.	

These figures refer to one class of land, the Bihar alluvium, and one cannot say what the corresponding proportions would be in other soils, but as there is extremely little information on this subject in the literature, the data will be of interest. It should also be noticed that although the volume of water increases during the rains to something like four times as much as in the dry season, the volume of gas does not generally decrease to one-half.

It will be a convenience for certain calculations to note that the percentage figures quoted in Table II. when multiplied by ten, become c.c. per c.dm. of soil.

Proportion of the gases dissolved in the soil-water.

It is evident that when the enclosed portion of soil is subjected to the vacuum as explained on page 89 of this memoir, not only will the gases which are present in the gas phase be pumped out, but also those which are present in the dissolved state in the aqueous solution will be extracted. Of the gases which are commonly present only one, carbon dioxide, is dissolved to any material degree. By way of illustration in respect of the other gases a high proportion of water may be assumed, *i.e.*, a condition when the amounts of dissolved gases are comparatively large. The soil interspace may be assumed as occupied one-half by water and the other half by atmospheric gases, carbon dioxide being excluded. Then :

	Vol.	O	N	A
(*a*) gas phase	1	20·93	78·10	0·937
(*b*) water	1	0·00607	0·0122	0·000337

from which it is evident that the amounts of O, N and A present in the soil-water are negligibly small. Carbon dioxide is much more soluble and is dealt with in the next paragraph.

The distribution of the amounts of CO_2 in solution and in the gas phase respectively.—A part of the carbon dioxide which is found in the mixed gases as obtained from soils is derived from the soil solution, the remainder being in the gas phase. The former is usually considerably greater than the latter, and it follows that to state the percentage of CO_2 present in the extracted gases without making due allowance for that part which is present in the soil solution would lead to a misapprehension as to the real state in the soil. For example, the analysis of a gas was found to be :—

N+A	.. ..	83·06 per cent.
O	.. ..	10·18
CO_2	.. ..	6·76

but calculation showed that of the 2·34 c.c. CO_2 which was measured, 1·965 c.c. was present in the soil solution, and only 0·374 c.c. was in the gaseous state. Consequently the real composition of the soil gases was :—

	%
N + A ..	.. 88·06
O ..	.. 10·80
CO_2 ..	.. 1·14

In order to be able to calculate the proportions of carbon dioxide in solution and in the gaseous state respectively, the following information is required :—

(*i*) The amount of aqueous solution in the soil and the solubility of carbon dioxide in this solution.

(*ii*) The volume of the gas phase.

(*iii*) The volume of CO_2 (total).

(*iv*) The relation between the partial pressure of CO_2 in the gas phase and in the solution.

(*v*) The temperature.

The mode of calculation involves two assumptions. The first is that the dissolved carbon dioxide is chiefly present as calcium bicarbonate. This involves no large error because calcium carbonate is the only carbonate which good soils contain in material quantity. The amount of alkali carbonates is usually so small that they cannot affect the question, and according to some recent work, magnesium carbonate is probably never present in material amount in good land.[1] Moreover calculation, to which reference is subsequently made (p. 106), shows that all ordinary soils contain much more than sufficient calcium carbonate to unite with any carbon dioxide which may be present in the soil.

The second assumption is that the carbon dioxide unites with calcium carbonate as quickly as the gas is formed. It would, it is true, be incorrect to speak of a state of true equilibrium occurring between the three phases for two reasons. (*i*) The aqueous solution must be assumed to be constantly moving from one point to another, either to supply a growing plant, or to replace water which has evaporated at the surface, or it is draining downward during wet weather. The actual distance through which such movement takes place is however small from the point of view now under

[1] J. Walter Leather & Jatindranath Sen. The system magnesium carbonate, calcium carbonate, carbonic acid, water. *Memoirs Dept. Agri. Ind., Chem. Series*, Vol. III, No. 8.
W. H. MacIntyre. The non-existence of magnesium carbonate in humid soils. *Agrl. Expt. Station of the University of Tennessee Bull.* 107, June 1914.

consideration; for example, the aqueous liquid probably never moves 0·5 inch per hour even in the wettest weather and usually the distance is very much less. (*ii*) Those gases such as carbon dioxide which are not at the same partial pressure in the soil as in the atmosphere, must be constantly subject to the process of diffusion, and consequently their quantity is always changing in the soil. Moreover it is probable that carbon dioxide is being formed over a large part of the year. But the fine state of sub-division and consequent great surface of contact between gas, water, and soil ensures that a state approaching equilibrium between the carbon dioxide and calcium carbonate must occur.

The relation between the partial pressure of the CO_2 gas and the CO_2 in $Ca(HCO_3)_2$ solution is known[1] and the following Table III contains the data necessary for our present purposes.

The volume of the liquid phase may be assumed equal to that of the water, but that of the gas phase is less than the volume of gases extracted, by the amount of carbon dioxide in solution.

TABLE III.

The relation between the carbon dioxide dissolved in $Ca(HCO_3)_2$ *solution and the superincumbent gas phase.*

CO_2 per 100 c.c. gas. p.p.	c.c. CO_2 per 100 c.c. $Ca(HCO_3)_2$ solution.		
	t = 20 °C.	t = 25 °C.	t = 30 °C.
0·1	1·31	1·35	1·39
0·2	2·01	1·97	2·04
0·3	2·59	2·57	2·55
0·4	3·10	3·04	2·99
0·5	3·57	3·47	3·39
0·6	3·98	3·85	3·74
0·7	4·38	4·22	4·07
0·8	4·77	4·57	4·38
0·9	5·13	4·83	4·68
1·0	5·45	5·19	4·97
1·5	6·99	6·57	6·22
2·0	8·42	7·77	7·28
3·0	10·80	9·84	9·09
4·0	12·95	11·66	10·60
5·0	14·85	13·30	12·05
6·0	16·60	14·78	13·33
7·0	18·30	16·15	14·50
8·0	19·90	17·50	15·63
9·0	21·35	18·70	16·67

[1] J. Walter Leather and Jatindranath Sen. The system calcium carbonate, carbonic acid, water. *Memoir Dept. Agri. Ind., Chem. Series*, Vol. I, No. 7.

The calculation for the distribution of the CO_2 between the two phases is then as follows :—

Put a = volume of water or aqueous solution
x = volume of CO_2 in unit volume solution
b = volume of gas phase
y = volume CO_2 in unit volume gas phase
then x : y = ratio of CO_2 in unit volume of liquid and gas phase respectively .. .. (1)
and ax + by = total volume CO_2 .. .. .. (2)

There are thus two unknowns, and equation(2) can only be solved after the solution of equation(1). But there is no direct solution for the latter. It can, however, be approximated : equation(2) can then be solved. From the information thus obtained a second approximation for equation(1) can be made and thence a second solution for equation(2). The true values of x and y can thus be obtained by a series of approximations. An example will illustrate the method :—

Volume of siliceous matter		..	..	82·6 c.c.
Do.	water	..	..	38·0 c.c.
Do.	gas	..	..	35·6 c.c.
Do.	CO_2	..	..	2·34 c.c.

Temperature 30 °C.

The first operation is to guess a first solution of equation (1). The CO_2, 2·34 c.c., is distributed between the 38 c.c. of soil solution and the 35·6 c.c. of gas. The two latter are approximately equal. Reference to Table III shows that with a p.p. = 1·5, 100 volumes of gas plus 100 volumes of solution would contain 1·5 + 6·22 volumes of CO_2 which is relatively greater than that present in the quoted case. Also it is evident that much the greater part of the CO_2 is derived from the solution. This mental estimate shows that the p.p. was $< 1{\cdot}5$. Equation (1) may therefore be solved with the values :

$x : y = 6{\cdot}22 : 1{\cdot}5$, whence $x = 4{\cdot}14\ y$.

and $x : y = 4{\cdot}97 : 1$, whence $x = 4{\cdot}97\ y$.

Employing the first in eq. 2 we have :—

$38\ x + 35{\cdot}6\ y = 2{\cdot}34$

$(38 \times 4{\cdot}14)\ y + 35{\cdot}6\ y = 2{\cdot}34$

$y = 0{\cdot}01215\ ;\ x = 0{\cdot}0502$

$ax = 1{\cdot}91$ c.c. CO_2 in solution

$by = 0{\cdot}43$,, ,, ,, gas

and the p.p. $CO_2 = \dfrac{0{\cdot}43 \times 100}{35{\cdot}6} = 1{\cdot}2$

Employing the second value in equation (2) we obtain

$$y = 0{\cdot}0104$$

and the p.p. $CO_2 = 1{\cdot}04$

It may be pointed out here that the value of y multiplied by 100 = the p.p.CO_2 in the gas phase.

The criterion of the correctness of the calculation is the equality of the partial pressure thus found from equation (2) with that which has been employed in equation (1). Thus in this example it is evident that the second value, *viz.*, 1·0 is much the better, and that 1·04 for the p.p. CO_2 is very near the truth. The distribution of the 2·34 c.c. CO_2 is then very nearly :—

0·37 c.c. in the gas phase
1·96 c.c. in the soil solution.

These values would not be materially different if a further approximation were made in which b is put equal to 35·6—1·96 = 33·64.

The analysis of the gas had yielded the following :—

	%
N + A ..	.. 83·06
O ..	.. 10·18
CO_2 ..	.. 6·76

But after distributing the CO_2 between the gas and liquid phases, the composition of the gas phase as it existed in the soil becomes :—

	%
N + A ..	.. 88·0
O ..	.. 10·8
CO_2 ..	.. 1·2

Another example may be taken :—

Volume of siliceous material	75·8 c.c.
Do. water	52·4 „
Do. gas	29·4 „
Do. CO_2	2·93 „

t = 30°C.

Here not only is the volume of CO_2 small, but the liquid phase is considerably greater than the gas phase, and it is evident that most of the CO_2 is present in the liquid.

If the p.p. CO_2 is put = 1
then $x : y = 5 : 1$ .. .. .. (1)
and $52{\cdot}4\ x + 29{\cdot}4\ y = 2{\cdot}93$ .. .. (2)

substituting

$$(52{\cdot}4 \times 5)\ y + 29{\cdot}4\ y = 2{\cdot}93$$
$$y = 0{\cdot}0100$$
$$x = 0{\cdot}0500$$

whence

$52{\cdot}4 \times 0{\cdot}05 = 2{\cdot}620$ c.c. CO_2 in solution
$29{\cdot}4 \times 0{\cdot}01 = 0{\cdot}294$ c.c. CO_2 in gas

$$\text{p.p. } CO_2 = \frac{0{\cdot}294 \times 100}{29{\cdot}4} = 1{\cdot}00$$

If, however, the p.p. CO_2 be assumed = 2, then x : y = 7·33 : 2 and the calculation yields

$$52{\cdot}4 \times 0{\cdot}0485 = 2{\cdot}54$$
$$29{\cdot}4 \times 0{\cdot}0132 = 0{\cdot}39$$

$$\text{and the p.p. } CO_2 = \frac{0{\cdot}39 \times 100}{2{\cdot}93} = 1{\cdot}32$$

instead of the p.p. 2 assumed.

Thus the first calculation is much the more correct and is in fact very near the truth.

The analysis of the gas in this example yielded :—

	%
N+A	79·0
O	10·9
CO_2	10·1

After deducting the CO_2 which was in solution, the composition of the gas phase in the soil becomes :—

	%
N+A	86·9
O	12·0
CO_2	1·1

The composition of the soil gases in the examples quoted in succeeding paragraphs are as found by the analysis of the gas as extracted from the soil specimens, and consequently the percentage of carbon dioxide is generally very much higher than was actually present in the gas phase in the soil. It has been considered preferable to leave the analyses thus unaltered, largely because so little is known regarding the respective functions of the dissolved and gaseous carbon dioxide. The following examples of re-calculated analyses will serve to illustrate the differences which exist between the percentage of total and gaseous carbon dioxide respectively.

TABLE IV.

Examples illustrating the percentage of total carbon dioxide and the same after correction for the part which is in solution.

	I	II	III	IV	V
	Composition found by gas analysis.				
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Nitrogen plus argon ...	76·47	80·45	77·36	80·78	74·50
Oxygen	13·56	7·25	6·85	2·23	4·36
Carbon dioxide ...	9·97	12·30	15·79	16·99	21·14
	Composition after correction for the dissolved carbon dioxide.				
Nitrogen plus argon ...	83·24	90·78	90·21	92·45	89·81
Oxygen	14·77	8·17	7·99	2·56	5·25
Carbon dioxide ...	1·99	1·05	1·80	5·00	4·94

Where the total carbon dioxide is much less than 10 per cent and the soil is not particularly dry it is nearly all in solution.

What proportion of $CaCO_3$ in the soil is necessary to satisfy any probable proportion of CO_2 as $Ca(HCO_3)_2$? In a foregoing paragraph (page 101) it has been mentioned that calculation shows that all ordinary fertile soils contain sufficient calcium carbonate to form the bicarbonate with any carbon dioxide which may occur in a soil.

The highest percentages of CO_2 which have been met with are (*i*) 15·79% in some green-manured soil, and (*ii*) 21·14% in the gases from the neighbourhood of the roots of an indigo crop.

For the present calculation the following assumptions will be made :—

(*i*) CO_2 in gas = 25%

(*ii*) temperature 30°C.

(*iii*) 1 c. dm. of soil to include :—

	c.c.
Siliceous material ..	500
Water	300
Gases	200
including CO_2 ..	50

that is, conditions requiring an unusually high proportion of calcium carbonate

The distribution of CO_2 works out to :—

11·7 c.c. in the gas phase.

38·1 c.c. in the liquid phase.

This carbon dioxide is equivalent to 0·153 grm. $CaCO_3$.

The 500 c.c. of siliceous soil material is equivalent to 1,350 grm., and 0·153 grm. of calcium carbonate is equivalent to 0·0113 per 100 dry soil. As all good arable soils contain more than this amount, and conversely an unusually high proportion of carbon dioxide has been assumed in the foregoing calculation, it may be safely concluded that all good soils contain more than sufficient calcium carbonate for the end in view.

Proportions of Oxygen and Carbon Dioxide in the Soil Gases in Fallow Land.

In Table V are set out a number of examples illustrating the proportions of oxygen and carbon dioxide which have been found in the soil gases of unmanured fallow land and a number of others will be found in Table XIII (page 119). There are several points of interest.

(*a*) The percentage of oxygen is considerably higher in the hot dry season (April to May) than during the monson (June-July). The percentages naturally vary but approximately the oxygen percentage was found to fall from say 16 or 18% in the dry season to between 8 and 12% during the rains.

(*b*) As is evident from the quoted examples, the percentage of carbon dioxide varies within wide limits, and there seems to be as much at 5 or 6 ft. deep as in the surface soil ; it increases during the monsoon but the change was marked chiefly after the first heavy rain. This point will be referred to subsequently when speaking of the changes during nitrification, but there seems to be no doubt that one of the effects of the first heavy rain is to occasion a production of this gas. The amount of carbon dioxide found in fallow land is, however, smaller than what I have met with in the neighbourhood of the roots of crops to which reference will also be made subsequently.

(*c*) It has been suggested by Wollny[1] that the sum of the percentages of oxygen and carbon dioxide in soil gases always approximates to 21, but this is far from being the case, and although the sum of the two often approaches this figure, there are too many exceptions to admit of this suggestion carrying any weight. The formation of carbon dioxide is doubtless dependent on the presence of oxygen, but to suggest that each volume of carbon dioxide which is formed demands one volume of oxygen would be a mistake. More exact information regarding this point is given when speaking of nitrification.

[1] *Expt. Stats. Record* IV. p. 537.

Table V.

Fallow land—unmanured. Proportions of oxygen and carbon dioxide.

Depth	1907 April 24th to May 8th.		1911 June 7th to 15th.		1911 June 27th to 29th.		1911 July 12th to 15th.		1908 Jany. 8th to 11th.	
Inches	O %	CO_2 %	O %	CO_2 %	O %	CO_2 %	O %	CO_2 %	O %	CO_2 %
0″—3″	...	...	...	...	...	...	...	...	.	...
3″—6″	17·2	2·9	...	..	...	...	...	...	...	...
6″—9″	16·2	5·9	...	...	...	...	...	...	...	...
9″—12″	18·6	3·6	...	...	12·7	12·0	...	.	17·5	4·3
1′0″—1′3″	17·4	8·5	9·8	3·9	...	...	12·0	4·4	...	...
1′3″—1′6″	...	...	..	...	...	...	...	...	...	...
1′6″—1′9″	...	...	...	...	...	...	...	...	...	...
1′9″—2′0″	...	...	..	...	9·2	6·9	...	...	18·5	5·4
2′0″—2′3″	17·7	4·6	14·6	1·9	..	...	9·8	3·4	...	...
2′3″—2′6″	..	...	...	...	..	...	...	...	...	...
2′6″—2′9″	...	.	..	...	..	...	...	..	...	...
2′9″—3′0″	17·6	5·9	...	...	9·7	6·0	...	...	17·6	6·9
3′0″—3′3″	13·8	7·0	8·9	1·4	...	...	7·6	5·4	...	...
3′3″—3′6″	...	...	...	...	...	...	...	...	...	...
3′6″—3′9″	...	...	...	...		..	...	...	...	...
3′9″—4′0″	17·8	3·1	...	...	...	...	...	...	...	...
4′0″—4′3″	...	..	14·9	2·7	...	...	11·9	4·1	13·3	7·0
4′3″—4′6″	..	...	...	...	...	.	...	...	...	...
4′6″—4′9″	.	...	..	.	...	...	...	..	...	..
4′9″—5′0″	13·4	8·5	...	...	...	...	...	...	...	..
5′0″—5′3″	...	...	12·7	6·1	...	...	..	...	..	...
5′3″—5′6″	...	...	...	...	...	...	...	.	...	...
5′6″—5′9″	...	...	...	...	...	...	...		..	...
5′9″—6′0″	...	..	...	...	...	...	...	..	...	...
6′0″—6′3″	15·5	8·2	...	...	...	...	...	...	...	...
	After long period of dry weather.		After 5·5″ of rainfall in preceding week which was absorbed by upper 2ft. of soil.		After 5·3″ of rain in 2 weeks.		After 5·5″ of rain in 2 weeks.			

Proportions of Oxygen and Carbon Dioxide in Manured Land.

A few samples of soil from land which had been manured with 20 tons of farm manure per acre were examined in 1907, and the percentage of oxygen and carbon dioxide found in the gases are set out in Table VI. The manure was applied on October 2nd and the samples were taken between October 6th and 8th and between December 21st and 24th, that is about 4 days and 11 weeks subsequently. There was some increase in the percentage of carbon dioxide, though the amount found eleven weeks after applying the manure was not very large. The number of tests was however small.

More striking is the fact that the gas of the soil some feet deep is as rich in carbon dioxide as the stratum of soil into which the manure was mixed. No doubt more carbon dioxide is formed in the latter, but being near to the surface it is enabled to pass readily into the outside atmosphere by diffusion and its concentration is thereby maintained at a low figure.

Table VI.

Composition of gas in fallow land after an application of 20 tons farmyard manure. Applied October 2nd. 1907.

Depth.		1907 October 6th to 8th.		1907 December 21st to 24th.	
Cm.	Inches	O %	CO_2 %	O %	CO_2 %
22·8—30·5	9″—12″	11·38	1·98	14·7	6·8
53·4—61·0	1′9″—2′0″	...		14·7	7·4
83·8—91·5	2′9″—3′0″	13·20	5·00	13·6	10·0
122·0—129·6	4′0″—4′3″	...	...	17·8	4·3

The Composition of the Gas in Green-manured Land.

Tables VII and VIII contain examples of the composition of the gases found in fallow land shortly after green-manuring. Those in Table VII were obtained from single borings, each of which had a volume of 0·154 c.dm. of soil. Moreover, the weight of green manure ploughed in was not known. The samples referred to in Table VIII are the result of a more carefully controlled experiment and the gas was more completely analysed. In this case the green crop—san hemp—(*Crotalaria juncea*) was taken from an area of 4 sq. yds., cut up rapidly in a chaff cutter, then distributed as uniformly as possible over the surface of the plot from which it was cut, and

dug in. For the gas analysis, six borings aggregating 0·926 c.dm. of soil, were taken for each sample, 3, 6, and 9 days respectively after digging in the green plant, which naturally provides a more reliable index of the general composition of the soil gases as a whole than would single specimens.

TABLE VII.

Fallow land after green-manure. Proportions of oxygen and carbon dioxide.

DEPTH.		San hemp ploughed in July 14th. Analyses made July 18th to 24th.		*Dhaincha* ploughed in August 5th. Analyses made August 8th and 14th.	
Cm.	Inches	O %	CO_2 %	O %	CO_2 %
15·3—22·8	6″—9″	10·9	10·1	10·6	18·4
22·8—30·5	9″—12″	11·9	6·3	10·1	8·0
30·5—38·1	1′0″—1′3″	10·1	6·8	...	...
61·0—68·6	2′0″—2′3″	12·5	3·5	...	...
91·5—99·1	3′0″—3′3″	12·0	4·0	...	...
122.0—129.6	4′0″—4′3″	10·0	5·1	...	...

TABLE VIII.

Composition of gas from green-manured land. Dug in September 11th, 1914.

Date		14-9-14.	17-9-14.	20-9-14.
Depth cm.		7·6—15·3	7·6—15·3	7·6—15·3
,, inches		3″—6″	3″—6″	3″—6″
Volume of gas per c.dm. of soil.		c.c. 214·7	c.c. 107·1	c.c. 159·5
		Per cent.	Per cent.	Per cent.
Nitrogen		78·42	82·70	76·43
Oxygen		7·48	8·81	6·85
Carbon dioxide		13·06	7·25	15·79
Hydrogen		*Nil*	·21	*Nil*
Methane		*Nil*	*Nil*	*Nil*
Argon		1·043	1·032	0·935
$\frac{N}{A}$		75	80	81·5
$\frac{O}{A}$		7·1	8·5	7·2
Rainfall notes		0·15″ rain on previous evening.	0·03″ on 14th and 1·31″ rain on evening of 16th.	No further rainfall.

It will be seen that the volume of gas obtained on the three dates varies considerably, a variation which is associated with the rainfall. Before September 14th there had been practically dry weather for 10 days. On the evening of 16th September 1·31 in. of rain fell and its effect by the following morning was to reduce the amount of gas from 214 c.c. to 107 c.c. per c.dm. in the surface soil temporarily. No more rain fell before 20th September with the natural result that a considerable increase of gas was found on the latter date. It would be unreasonable to conclude from a single experiment that the rainfall of the 16th caused a decrease in the amount of carbon dioxide such as the figures indicate. It is, however, evident from the presence of hydrogen gas after the somewhat heavy rain of 16th that other changes set in temporarily.

Regarding the nitrogen, it has been thought probable that this element is frequently set free from its combined state in manures by bacterial agency. The subject is referred to for instance by Russell[1] who deduces a considerable annual loss from land at Rothamsted on which large amounts of farm manure had been annually applied for 40 years.

An estimate of the amount of organic nitrogen which the green manure contained was made from the weight and analysis of the plant growing on the next neighbouring ground, and which came to 0·0886 grm. N per sq. dm. of surface. The object in view had been to compare this with any excess of nitrogen which the analysis of the soil gases might indicate, and hence form an estimate of what proportion (if any) of the nitrogen in the green manure had been set free in the elementary state. It is true that the analyses actually show an increase of nitrogen during the period, the N : A ratios being 75, 80, 81·5 respectively. But these differences lie within the experimental error (see page 95), and the apparent increase must be referred to this cause.

As a matter of fact the nitrogen in green manure is small compared with the nitrogen gas commonly present in the soil. Thus, in the experiment under reference, the weight of green plant was about 8 tons per acre. The total nitrogen in it was equal to 0·0886 gram per 1 sq. dm. of surface. Assuming that the material is uniformly distributed throughout the upper 1·5 dm. (6 inches) of soil, the comparison may be made between the volume of nitrogen gas present in the soil and the nitrogen (combined) of the green manure. The former was (on September 14th and assuming that the first 3 inches of soil contained the same amount of gas as the second 3 inches) 255 c.c. whilst the latter is equal to 71 c.c. N per 1·5 c. dm. of soil. Thus

[1] E. J. Russell, *Soil conditions and plant growth*, p. 82.

supposing one-tenth part of the nitrogen of the green manure were liberated as gas, it would not alter the $\frac{N}{A}$ ratio sufficiently to admit of its detection, unless the experimental error were reduced considerably below what I have commonly found.

An experiment was made in a closed vessel of known volume, in which 100 grm. air-dry soil + 1·0 grm. green leaf of *Poinciana regia* (gulmohr) + about 19 grm. water were allowed to stand for 15 days at room temperature (about 30 C) ; the gas was then pumped out and analysed. The following are the data :—

100 grm. air-dry soil (D=2·71)	36·9 c.c.
19·2 grm. water	19·2 ,,
1 grm. leaf	1·0 ,,
Damp air at 29°C	1656·3 ,,
Volume of flask	1713·4

1656·3 c.c. damp air at 29°C equals 1429·1 c.c. dry air N.T.P.

	Initial	Final
N+A	1129·6 c.c.	1134·1 c.c.
O	299·1 ,,	187·68 ,,
CO_2	0·43 ,,	96·23 ,,
	1429·1	1418·01

The difference between the volumes of N+A initially present and found when the gases were pumped out is 4·5 c.c. This may be due to one or both of two causes, (*i*) inaccuracy in the estimate of the original volume of air, and (*ii*) the evolution of N. gas from the organic matter. As to the first it is derived from the difference :—

Volume of flask − (volume of soil + volume of green leaf + volume of water) each of which is known with considerable accuracy. But it had to be assumed that the air in the flask was fully saturated with moisture when the flask was closed. If the relative humidity had been 90 % instead of 100 % as assumed, then the volume of N+A in the enclosed air would have been 1134·0 c.c. It is not likely that the humidity was actually so low as 90 %, but it is well known that to fully saturate a gas in a flask of 1·5 litre capacity without agitation requires some little time, and consequently that a part, at least, of the difference between the estimated initial N+A and that measured at the conclusion of the experiment was due to this source of error.

It is therefore to be concluded that either no nitrogen was liberated in the elementary state, or that its volume was small.

The Gases of Swamp Rice Land.

The conditions under which "wet" paddy grows is a theme which Harrison and Subramania Aiyer have dealt with at some length[1] and the investigation is still in progress. In the first of these contributions it was pointed out that the nitrogen in the evolved gases must be derived from one or all of three sources; (*a*) the gases present in the soil at the time when the land is submerged for paddy cultivation and which therefore is in part imprisoned, (*b*) the atmospheric nitrogen which is dissolved in the irrigation water, (*c*) the organic nitrogenous substance of the soil and green manure. Measurements of the amount of nitrogen evolved from plots showed that this was very considerably greater from manured than from un-manured land, and this result was substantiated by pot-cultures. The inference was therefore made that a part at least of the gaseous nitrogen was derived from the green manure. Direct evidence was nevertheless very desirable and Mr. Harrison sent me samples of these gases in 1914 in order to determine the N : A ratio. The analyses are set out in Table IX.

Table IX.

Composition of gas from swamp rice land.

	A.	B.	C.
Nitrogen	84·25	86·60	85·91
Oxygen	0·32	0·31	0·99
Carbon dioxide	4·34	4·23	4·69
Hydrogen	8·81	3·91	4·53
Methane	1·37	4·06	3·00
Argon	0·915	0·885	0·879
$\frac{N}{A}$	92	98	97

A glance at the N : A ratios shows that these are so high that there is no doubt at all that nitrogen has been liberated. Under the conditions of the cultivation of this crop atmospheric air is very largely excluded, and the argon present is necessarily largely obtained from the gases dissolved in the irrigation water. The ratio N : A dissolved in water when freely exposed to the air is 33·8 at 30°C, and if no nitrogen were obtained from other sources, these two elements would be present in the paddy land gases in a proportion not widely different from this. If, for example, one volume of water saturated with air were shaken with an equal volume of gas containing neither nitrogen nor argon, the N,A ratio in the gas phase would become 33·5; if the one volume of water were shaken with one-tenth its

[1] *Mem., Dept. Agri. Ind., Chem. Series*, Vol. III, No. 3, & Vol. IV, No. 1.

volume of other gas, the N/A ratio would be 39 (assumed temperature = 30°C.) There can therefore be no doubt that a high proportion of the nitrogen found in these gases is derived from the soil and manure.

The Gases Present in the Neighbourhood of the Roots of Crops.

A number of samples of gas from the neighbourhood of crop-roots have been examined. It may be mentioned that the original object in view was to try to ascertain whether the assimilation of elementary nitrogen by a papilionaceous crop could be detected by the aid of the N : A ratio, although it had to be realized at the outset that the amount of nitrogen thus disappearing from the soil gases was probably too small to admit of its detection. Apart from this, the examination of these gases is of considerable interest in other respects, for the amounts of oxygen are unexpectedly small, those of carbon dioxide very large, and the presence of hydrogen had not been suspected.

Referring to the amount of nitrogen assimilated by a papilionaceous crop, the following is an estimate showing the relation between the combined nitrogen in the crop and the gaseous nitrogen in the soil respectively. Employing san hemp as an example, the amount of nitrogen found in several samples in July 1914 varied from 50 to 70 lb. per acre. Assuming 60 lb. as an average quantity, this is equivalent to 0·0672 gram per sq. dm. of soil surface. It is by no means the case that all the nitrogen of these crops is usually assimilated from the elementary state,[1] and it is moreover still quite uncertain whether the assimilation takes place through the roots or through the above-ground parts of the plant, though most authorities favour the former view. But assuming merely for the purposes of the present calculation that the whole of the nitrogen of the crop is assimilated through the root system and that it is obtained entirely from the gaseous nitrogen of the upper two feet of soil, the comparison becomes between the quantity 0·0672 gram nitrogen in the crop and the elementary nitrogen which is in say the upper two feet or 6·1 decimetre of soil. The data contained in Table X indicate that 1 c.dm. of the Pusa soil usually includes during the monsoon say 0·150 to 0·200 c. dm. of gas containing say 80% nitrogen. The temperature may be assumed to be about 30°C. Thus in the upper two feet, or 6·1 decimetre of soil there may be expected to be at least some 0·732 c. dm. nitrogen in 6·1 c. dm. of soil. This quantity of nitrogen would weigh 0·821 grm. We have then the relation 0·821 : 0·0672 and it becomes apparent that even on the excessive assumption employed, the amount of nitrogen assimilated would

[1] Lawes & Gilbert, *J. R. A. S. E.*, 3rd Series, Vol. II, p. 696.

TABLE X.

Composition of gas from the soil near the roots of crops.

Date	San hemp (*Crotalaria juncea*)				Indigo (*Indigofera arrecta*)			Maize (*Zea mays*)			
	27-7-14	30-7-14	3-8-14	25-8-14	18-8-14	20-8-14	23-8-14	4-9-14	6-9-14	8-9-14	10-9-14
Depth cm. ...	7·6- 5·2	15·2-22·8	30·5-38·1	7·6-15·2	7·6-15·2	15·2-22·8	30·5-38·1	7·6-15·2	15·2-22·8	30·5-38·1	7·6-15·2
„ inches ...	3″—6″	6″—9″	12″—15″	3″—6″	3″—6″	6″—9″	12″—15″	3″—6″	6″—9″	12″—15″	3″—6″
Volume of gas per 1 c. dm. soil ...	c.c. 250·0	c.c. 195·4	c.c. 149·3	c.c. 224·1	c.c. 134·9	c.c. 212·0	c.c. 177·4	c.c. 54·93	c c. 146·5	c.c. 193·9	c.c. 158·9
Nitrogen ...	% 79·77	% 83·73	% 85·05	% 81·63	% 79·99	% 72·96	% 82·26	% 81·59	% 82·59	% 76·94	% 79·47
Oxygen ...	2·23	5·81	9·00	1·67	5·21	1·36	3·33	13·82	6·28	8·65	7·25
Carbon dioxide ...	16·99	9·36	4·84	12·12	13·80	21·14	12·62	3·34	8·71	12·08	12·30
Hydrogen ...	.....	.....	.....	0·582	.....	0·637	0·743	0·18	1·39	1·37	*Nil.*
Methane .	.....	.....	... .	*Nil.*	.....	*Nil.*	*Nil.*	*Nil.*	*Nil.*	*Nil.*	*Nil.*
Argon ...	1·010	1·101	1·111	0·999	0·967	0·906	1·041	1·073	1·028	0·956	0·981
N A ...	79	76	76	82	83	80	79	76	80	81	81
O A ...	2·2	5·3	8·1	1·7	5·4	1·8	3·2	12·9	6·1	9·6	7·4
Rainfall notes ..	Last heavy rain July 15th.	No more rain.	4·17″ in 4 days.		Last heavy rain Aug. 14th.	No more rain.	No more rain.	15·27″ in preceding 9 days.	No more rain.	No more rain.	0·11″ more rain.

be only small in comparison to the whole gas present. When further it is recollected that the nitrogen of the crop is assimilated in part as combined nitrogen, that the portion assimilated is taken up gradually during several months, that any reduction in the nitrogen partial-pressure would be constantly rectified by the agency of diffusion from the atmosphere, it becomes certain that the actual effect of nitrogen assimilation by these crops on the N : A ratio will be so small as to demand for its detection a much higher degree of accuracy than I have been able to attain with small volumes of gas, if indeed it could be detected in this manner at all.

After finding the frequently low proportions of oxygen and high proportions of carbon dioxide, in the earlier samples, it was thought possible that hydrogen or methane might be present, and the result of the examination for these gases showed that although no methane or other hydrocarbon was met with, hydrogen is a common constituent. The quantities are small, but are nevertheless quite definite. This gas was found in the neighbourhood of the roots of all the three crops, san hemp, indigo and maize. The composition of these gases possesses perhaps the most interest of any. We are unfortunately very ignorant at the present day of the nature of the lower organisms which accompany the development of higher plants, but the idea of certain specific associations between higher plants and soil organisms naturally presents itself as probable. It may be assumed as highly improbable that hydrogen is liberated by the higher plant, and indeed it is doubtful whether such experimental evidence as exists is sufficient to prove that carbon dioxide is thus produced. So far as I am aware, the proof of the production of carbon dioxide by the roots of crops rests on experiments made in the presence of other lower forms of plant-life and which latter are known to be a source of carbon dioxide.

Nitrification.

In a memoir of this series dealing with some records of drainage, three circumstances among others in respect of soil nitrates were referred to, namely : (*i*) the difference between the amounts of nitrate, obtained from the drain-gauges of cropped and fallow soil respectively, was much greater than could be accounted for by simple crop assimilation[1] ; (*ii*) energetic nitrification occurred in fallow soil immediately after the first heavy rain of the monsoon[2] ; (*iii*) the amount of nitrate then formed is so great, that the

[1] *Mem., Dept. Agri. Ind., Chem. Series*, Vol. II, No. 2, p. 94.

[2] *Ibid.*, p. 101.

equivalent amount of oxygen is nearly equal to and in some cases has exceeded that which would be present in the soil in the gaseous state,[1] or alternatively as oxygen and carbon dioxide, since the latter gas is closely associated with nitrification.

Principally in order to try to gain a knowledge of the proportions of oxygen and carbon dioxide gases which are present during a period of intensive nitrification, some special tests were made in June 1914, which will be referred to presently. Incidentally, however, some further information was gained regarding the other two points and this may be suitably referred to here.

Nitrification is especially active in fallow soil immediately after the first heavy monsoon rainfall.—This has proved to be uniformly the case, as the figures in the subjoined table show :—

TABLE XI.

Pounds (avoir.) of nitric-nitrogen per acre × ½ foot, in fallow land.

DEPTH		1910			1911			1914		
Cm.	Inches	25th May		18th June	4th May		10th June	30th May		24th June
		lb.	3·71″ rain.	lb.	lb.	4·66″ rain.	lb.	lb.	1·21″ rain.	lb.
0—15·2	0″— 6″	1·20		3·30	1·37		1·97	9·48		3·44
15·2—30·5	6″—12″	0·66		18·31	1·58		18·95	0·71		22·20

Rainfall 1910 : principally 0·78″ on June 1st.
2·15″ on June 15th.
0·29″ on June 16th.
0·94″ on June 17th.

Do. 1911 : principally 0·25″ on June 5th.
0·80″ on June 6th.
2·31″ on June 8th.

Do. 1914 : principally 1·32″ on June 9th.
1·71″ on June 17th.

Effect of a crop on nitrification.—The evidence on this subject which was offered in the memoir on drainage consisted in a comparison between the

[1] *Mem., Dept. Agri. Ind., Chem. Series*, Vol. II, No. 2, p. 116.

amounts of nitric-nitrogen found in the drainage waters from fallow-soil and cropped-soil respectively. Some further evidence was met with in 1914. Wheat had been cultivated during the cold-weather of 1913-14 on one half of a plot of land (the whole of which had been "green-manured" with san hemp in 1913) and had been harvested early in April, after which this portion of the land was also well cultivated with the hoe; that is to say, one half the plot had been green-manured and then left fallow for nine months, whilst the other half had been green-manured, had borne a crop of wheat, and had then been fallow for two months. Determinations of the nitrate in the soil were made before and after the first heavy monsoon rain, when it was found that where the wheat crop had grown, hardly any nitrification had occurred, as the following Table XII shows:—

TABLE XII.

Pounds (avoir.) of nitric-nitrogen per acre × ½ foot, after fallow and wheat respectively.

DEPTH		AFTER FALLOW			AFTER WHEAT		
Cm.	Inches	30th May	Rainfall inches	24th June	30th May	Rainfall inches	24th June
		lb.		lb.	lb.		lb.
0—15·2	0″— 6″	9·48	4·21	3·44	1·32	4·21	4·91
15·2—30·5	6″—12″	0·71		22·20	0·42		1·97

In the Memoir on Drainage (p. 97) the conclusion was drawn that the deficiency of nitrate in the drainage water after crops (wheat and maize) was, of three possible causes, most probably due to an effect of the higher plant on soil organisms. The experiment of 1914 now quoted also supports this view. It is true it might properly be suggested that the wheat crop had drawn on the store of readily nitrifiable matter in the soil to such an extent as to leave but little for immediate nitrification; but against this being the probably correct explanation is the fact that the Pusa soil yields comparatively large amounts of nitrate annually when fallow and without the aid of any manurial substance, *i.e.*, the amount of nitrate formed in the Pusa soil is large when no manure has been used. For example, the amount of nitrate formed in June 1914 after green-manuring is not very different from the amounts formed in 1910 and 1911 after the simple fallow (*See* Table XI).

The composition of the soil-gases during nitrification.—In 1914 the gases contained in the soil, "after fallow," referred to in Table XII. both before and after the first heavy rain of the monsoon, were extracted, measured and analysed. It was anticipated that an abundant nitrification would occur, which anticipation was realized. The amount of nitrate quoted is the mean of four samples in each case. For the gas analyses four specimens of the first three inches of soil were examined at the end of May, and two specimens were examined for each of the other depths. The mean of these analyses are quoted in the subjoined Table XIII :—

TABLE XIII.

The composition of the gas in fallow land before and after nitrification.

Date	Depth		Nitrogen %	Oxygen %	Carbon dioxide %	Argon %	Ratio	
	Cm.	Inches					$\frac{O}{A}$	$\frac{N}{A}$
May 30th ...	0— 7·6	0″—3″	78·45	20·44	0·12	0·988	20·6	79
June 1st ...	7·6—15·2	3″—6″	78·44	20·30	0·25	1·007	20·2	78
June 2nd ...	15·2—22·8	6″—9″	77·08	20·29	1·65	0·976	20·8	79
June 3rd ...	22·8—30·5	9″—12″	78·21	20·56	0·29	0·937	22·0	84
			Rainfall—4·21″.					
June 19th and 20th	0— 7·6	0″—3″	78·43	19·64	0·97	0·954	20·5	82
	7·6—15·2	3″—6″	78·85	19·67	0·56	0·923	21·4	85
	15·2—22·8	6″—9″	79·10	18·99	0·94	0·967	19·7	82
	22·8—30·5	9″—12″	78·95	18·75	1·32	0·978	19·2	81

NOTE.—Rainfall included principally :—1·32″ on June 9th, 0·75″ on June 11th, and 1·71″ on June 17th.

These figures were not what I had anticipated. The amount of nitrate which had formed so quickly demanded a considerable consumption of oxygen—directly or indirectly—whilst actually the effect on the proportion of this constituent is only nominal. Any reduction in the proportion of oxygen would naturally set up diffusion of this gas from the atmosphere, but this process has been usually looked upon as only a very slow one. It was evident at least that measurements in the field did not add much to our knowledge of the quantities of either oxygen or of carbon dioxide which are involved under the circumstances.

Recourse was then had to measurements of the gases in contact with soils contained in closed vessels. Two series of such measurements were made, (*i*) in vessels not much larger than sufficient to contain the soil, and (*ii*) in much larger vessels. The volume of air included in the former was somewhat (about one-third) greater than would be present in the natural soil; whilst in the latter series it was about seven times as great. In each case the slightly damped soil was packed carefully into the vessel so as to occupy approximately the volume it would do in the field, and a dilute solution (0·157 gram $(NH_4)_2SO_4$ per 100 c.c.) of ammonium sulphate was then gradually added dro by drop; this solution rapidly distributed itself throughout the soil. The vessel was closed with a paraffined cork and had also a tapped exit tube. These vessels were quite gastight under the conditions of the experiment. They were then incubated at 30°C. for about three weeks. Other portions of the same soils tested weekly in order to ascertain the rate of nitrification indicated three weeks as a suitable period to allow. When pumping the gases out of the vessels, the cork stoppers were submerged in water.

Respecting the estimation of the initial volume of air which was enclosed, this was derived from (*i*) the known volume of the vessel and its exit tube, (*ii*) the volume of the soil derived from its weight and specific gravity, (*iii*) the known volume of water added, (*iv*) the temperature of the air. The data are collected in the two following Tables XIV and XV. An examination of these two sets of data shows very clearly what occurred under the two different conditions. Where the total volume of air was only slightly more than what is actually present in the soil, substantially all the oxygen disappeared and a large amount of carbon dioxide was produced. The two volumes of these gases are by no means identical; in No. I that of carbon dioxide is considerably less than the oxygen which disappeared, in No. II they are approximately equal, in No. III the carbon dioxide is much in excess of the oxygen. At the same time all, or practically all, the nitrate which the soil originally contained disappeared. In the second series, where the volume of air was very much greater, there was again an almost complete utilization of oxygen, accompanied by the formation of a large quantity of carbon dioxide, the volume of the latter being however very much smaller than the oxygen which disappeared. At the same time a considerable amount of nitrate formed, this being in two cases more than 40 parts nitrogen per million parts of soil, which is higher than is commonly found in the field even under good conditions. The total volume of oxygen in the carbon dioxide and the nitrate is considerably less than that of oxygen which disappeared.

Table XIV.

The changes in the quantities of gases in contact with damp soil (small vessels).

	I		II		III	
Date of commencement	28-1-15		29-1-15		3-2-15	
Do. termination ...	22-2-15		17-2-15		22-2-15	
Soil, grm. ...	79		80		100	
Water ,, ...	12		11·6		14·1	
Air moist ...	45·2 c.c.		40·4 c.c.		56·95 c.c.	
Air, N. T. P. dry ...	40·95 c.c.		36·6 c.c.		51·59 c.c.	
	Initial %	Final %	Initia %	Final %	Initial %	Final %
N + A ...	79·07	85·67		80·73		73·92
O ...	20·93	0·35		0·13		2·00
CO_2 ...	...	13·98		19·14		24·08
	100·00	100·00		100·00		100·00
	Volumes		Volumes		Volumes	
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
N + A ..	32·38	34·26	28·94	31·37	40·79	11·82
O ..	8·57	0·14	7·56	0·05	10·80	1·21
CO ...	...	5·59	...	7·44	...	14·60
	40·95	39·99	6·60	38·86	51·59	60·63
	m. grm.	m. grm.	m grm.	m. rm	m grm.	m. grm.
Nitric-nitrogen ..	0·96	*nil*	0·96	*nil*	0·26	0·045

Table XV.

The changes in the quantities of gases in contact with damp soil (large vessels).

	I		II		III		IV	
Commenced ...	4-3-15		8-3-15		10-3-15		14-5-15	
Terminated ...	30-3-15		30-3-15		31-3-15		2-6-15	
Soil, grm. ...	100		100		100		100	
Water, grm. ...	15·2		14·1		14·5		13·8	
Air ...	257·6 c.c.		255·0 c.c.		241·3 c.c.		328·8 c.c.	
Equivalent to c.c. at N. T. P. ...	229·9 c.c.		223·94 c.c.		214·19 c.c.		277·3 c.c.	
	Initial %	Final %	Initial %	Final %	Initial %	Final %	Initial %	Final %
N+A ...	79·07	87·00		86·68		85·87		85·37
O ...	20·93	0·41		0·06		0·05		2·50
CO_2 ...	...	12·59		13·26		14·08		12·13
	100·00	100·00		100·00		100·00		100·00
	Volumes c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
N+A	181·8	181·14	177·00	181·09	169·30	167·79	219·20	222·65
O	48·1	0·85	46·87	0·12	44·83	0·10	58·04	6·52
CO_2	...	26·21	0·07	27·70	0·06	27·51	0·08	31·63
	229·9	208·20	223·94	208·91	214·19	195·40	277·32	260·80
	m. grm.	m. grm.	m. grm.	m. grm.	m. grm.	m. grm.	m. grm.	m. grm.
Nitric Nitrogen initial	1·24	2·79	0·19	4·86	0·67	4·77	0·17	4·05
Freshly formed ...		1·55		4·67		4·10		3·88
Equal to O ...		5·3		16·0		14·1		13·3
Equivalent Vol. ...		3·7 c.c.		11·2 c.c.		9·8 c.c.		9·3 c.c.

Regarding the nitrogen, denitrification and liberation of nitrogen gas may have occurred in the first series, but the figures cannot properly be employed as a proof of this because the volumes of nitrogen gas, equivalent to the nitrate which disappeared, (namely 0·77, 0·77, 0·17 c.c. respectively) are considerably smaller than the increased volumes of nitrogen *plus* argon. There is necessarily some error in computing the initial volume of air in the vessel, and to this must in part be referred the apparent increase of nitrogen gas.

These measurements of the oxygen and carbon dioxide not only illustrate the large amounts of these two gases which are involved, but also, when considered in conjunction with the composition of soil gases during a period of active nitrification in the field, (Table XIII) demonstrate the fact that diffusion of gases through soils is at least so rapid that the proportion of oxygen is maintained nearly equal to that in the atmosphere, whilst conversely that of carbon dioxide is maintained quite low. Regarding the very small proportion of oxygen which was finally present in the second series of laboratory experiments, it would naturally be a mistake to conclude that the nitrate was formed principally subsequent to the formation of the carbon dioxide; it may have formed whilst there was still much oxygen present. At the same time, whilst it is well established that the presence of oxygen gas is necessary to the process of nitrification, exaggerated ideas frequently prevail on this matter. Schloesing and Münz found that nitrification occurred when the superincumbent gas contained only 1·5 per cent. Moreover it is well established that the presence of free carbon dioxide, as well as a suitable base, is as essential as oxygen to this process.[1]

Diffusion of gases through soils.

The foregoing paragraphs provide information in respect of the composition of the gaseous mixture present in the soil at the particular time when the samples were taken, but do not indicate the amount of gaseous interchange which must be constantly in progress through the agency of diffusion between the soil and the atmosphere. For it will be readily appreciated that, for example, where the soil gas contains a higher percentage of carbon dioxide than is present in the air, this gas will tend to pass outwards; or if oxygen gas is being consumed in the soil, its proportion in the soil gas will be reduced below that in the atmosphere, and more oxygen will pass into the soil. Again, the result of these two processes may be to alter

[1] Lafar. *Handb. d. technische Mykologie*, pp. 163, 173.

the percentage of nitrogen: the decrease of oxygen may exceed the increase of gaseous carbon dioxide, and in such a case nitrogen would diffuse outwards. The same would apply to the argon.

It is usual to attribute the value of ploughing or harrowing the surface soil largely to the exposure of this soil stratum to the air; and when a green manure is dug or ploughed into the surface soil, the latter is left as loose as possible for the ready admission of atmospheric oxygen and the equally free escape of the carbon dioxide produced. Such a mental picture of the case is naturally readily assimilated, and questions regarding the soil 6 or 8 inches below the surface, and which is commonly never disturbed, do not necessarily trouble the agriculturist. As a matter of fact he knows that good cultivation of the surface soil is productive of good crops, and if he is told that the chief explanation for the advantage lies in the necessity for allowing atmospheric oxygen to enter or carbon dioxide to leave the soil, he naturally accepts it; the acceptance costs nothing and does not in any way affect his appreciation of good cultivation, which is based on outturn of crops. But the tests made in relation to nitrification brought the question of diffusion of soil gases very particularly into prominence, because these demonstrated that the process was at least so rapid that large amounts of oxygen from the atmosphere must have passed not only into the cultivated upper soil but also into the undisturbed soil below, and that the carbon dioxide produced escaped with equal facility.

Direct experimental evidence as to the rate of diffusion of gases through soils is apparently limited to that provided by E. Buckingham[1] who concluded that the quantity of gas diffusing depended *inter alia* on the soil "interspace" or "pore-space" occupied by gases, that is, in fact on that fraction of the total soil volume which is not occupied by either soil material or water; and he deduced the formula:—

$$D = K S^2 \triangle \quad \ldots\ldots\ldots\ldots\ldots\ldots (i).$$

in which D = the mass of gas diffusing in unit time through unit cross-section of soil.

K = the coefficient of diffusion for the particular gas.

S = the porosity of the soil.

$\triangle$ = the difference of partial pressure of the gas on the two surfaces. (*See* ii below).

[1] E. Buckingham. Contribution to our knowledge of the aeration of soils. *U. S. Dept. Agric. Bureau of Soils, Bull.* **25** (1904).

Thus the free diffusion which would occur between the gases if no soil were present, is controlled or reduced by the soil material and water. The whole volume of the soil is expressed as unity, and Buckingham gives the name "porosity" to that fraction of the whole volume of soil which is occupied by gas, a term which will be here adhered to.

The determination of the rate of diffusion of gases through soils is accompanied by more than usual difficulties and there is admittedly a want of good agreement among Buckingham's experimental data. Moreover the soils employed were filled into the apparatus and artificially packed: soils in their natural state would have been preferable. But after giving every weight to these points, one must conclude that Buckingham's experimental data are not so far removed from the truth as to be useless. The values which he obtained for the index (Equation 1) were in some cases approximately 1, in others nearly as high as 3, but the majority of the values approach 2 so closely that it may safely be employed for approximations regarding diffusion through soils. More than approximations are not possible for other reasons which will be subsequently referred to. Again as touching Buckingham's experimental data, although the soils were artificially packed, the degree of packing as represented by the porosity was quite similar to that which exists in nature. It is necessary when considering the reliability of these experimental data, to bear in mind that independent evidence of the reliability of the calculated quantity of a gas diffusing into or out of the soil is very difficult to obtain, and yet in the absence of such evidence, the result of any calculations of the quantities would only carry weight if the premises of the calculation were incontestably sound.

Buckingham's formula has been applied to certain of the previously quoted examples of soil gases, and the calculated quantities of gases diffusing per day can, in some of them, be compared with extraneous evidence. The quantities of gas so obtained have been transposed to *volumes* since these will be more readily appreciated than if they were expressed in terms of mass.

Before considering the data, it is desirable to refer to the various factors which in addition to the soil and its physical state control gaseous diffusion; these are as follows:

(*i*) The mass of gas diffusing naturally varies with both the cross-section and the length or thickness of the soil column as well as with the time period; these can be perfectly defined, and the units here adopted are c. dm. of gas per 1 dm. per 1 sq. dm. per day.

(*ii*) The mass of a gas diffusing depends on the difference between the pressure exerted by this gas on the one and the other end of the soil-column respectively. This pressure is called the partial pressure of this particular gas, when the total pressure of the gaseous mixture is equal on both sides of the soil-column. The total pressure in the case of soil gases may be assumed to be that of the atmosphere within very small limits. If the gaseous mixture contains say 1% of a certain gas, that gas is exerting $\frac{1}{100}$ part of the total pressure, and its partial pressure may be defined either as 1% or 0·01, or 0·76 cm. of mercury, according as the total pressure is defined as 100, or 1, or 76 cm. of mercury. For our purposes the total pressure is defined as 100. Thus if the soil gas at 1 dm. depth contained 1·03% CO_2 and the atmosphere contained 0·03%, the difference (Δ) would be 1, and the quantity of carbon dioxide passing out of the soil would be the $\frac{1}{100}$ part as much as would pass out if the gas in the soil were pure (*i.e.*, 100%) CO_2 and if the air contained none. This partial pressure difference is sometimes referred to as the gradient. Other things being equal, the quantity of a gas diffusing depends directly on this gradient. The unit adopted here is a gradient of 1% per 1 dm.

(*iii*) The quantity of gas diffusing depends finally on the temperature; it is facilitated by a rise of temperature, and other conditions being fixed, the quantity varies as $(1 + \alpha t)^2$. For present calculations a temperature of 30°C. has been adopted as being approximately representative of the conditions subsisting when the samples were taken.

(*iv*) The co-efficients of diffusion used are multiples of those determined by Obermayer[1] for the diffusion of O, CO_2, and H into air, and N into O respectively in order to agree with units here adopted.

But whilst the foregoing conditions are perfectly defined, those occurring in the soil must be regarded as changing so rapidly that it is quite impossible to define the latter very precisely. For example, consider the temperature. This will vary at 1″ from the surface in June from say 24° to 40°C. during the 24 hours. The variations in the deeper soil are less, until at 24″ deep the diurnal variation is negligibly small[2]. The effect of a temperature difference such as that near the surface would be to alter the rate of diffusion by about 12%, but since the temperature change decreases with the depth it cannot be defined for any particular soil stratum. By employing the mean temperature=30°C., the error due to temperature variation is reduced to much smaller dimensions

[1] Winkelmann. *Handb. d. Physik*, Vol. I, pp. 14—21.

[2] J. W. Leather. Soil Temperatures. *Mem. Dept. Agric. Ind. Chem. Series*, Vol. IV, No. 2, p. 36.

than are other probable errors. Again the absorption of oxygen, or the production of carbon dioxide being due to bio-chemical processes must be regarded as suffering constant change. The instances which will be here considered occurred generally between 3″ and 15″ deep in the soil, *i.e.*, where the diurnal temperature changes were comparatively small, but moisture conditions were in some cases suffering rapid changes, and these may have affected the rate of absorption or production respectively. Finally changes in water-content also occasion changes in the porosity. The nett result of such varying conditions is to show that, although the examination of the soil gases yields certain defined values for the partial pressure differences, these are in actuality constantly changing from hour to hour or from day to day in no small degree. A series of diffusion waves are thus set up in both directions which it would be impossible to define accurately. This is well illustrated by the examples to be quoted. Nevertheless for purposes of calculation it has been assumed that a certain gradient existed for a sufficiently long time to allow of the use of the foregoing equation.

The values of K are as follows :—

$K_N = 1{\cdot}903$
$K_O = 1{\cdot}892$
$K_{CO_2} = 1{\cdot}435$
$K_H = 6{\cdot}805$

} mass per sq. dm. per day through 1 dm. when p.p. $\Delta = 1\%$ and $t = 30^\circ C$.

A special remark applies to the carbon dioxide. It has been explained that a part of this compound is present as calcium bicarbonate, and a part in the simple gaseous state. It is only the latter which is subject to the laws of diffusion.

Turning now to examples, that relating to the conditions of nitrification (Table XIII) may be first considered. In this case oxygen was passing into the soil in part to produce carbon dioxide and nitrate and in part for other reasons which we know practically nothing of. These facts are well known,[1] but the amount of oxygen (in excess of the CO_2 and nitrate requirement) consumed by the Pusa soil in my experiments (Table XII) is very much greater than Dehérain and Demousy found (Russell unfortunately did not measure the volumes) and the supply of oxygen was not even then sufficient. During the period of nitrification in the field (June 1914), carbon dioxide was produced, some of which would pass into the form of calcium bicarbonate in solution, whilst another portion would diffuse outwards into the atmosphere.

[1] Dehérain et Demousy, *Ann. Agron.*, XXII (1906), p. 305. E. J. Russell, *J. Agri. Sci.*, I (1905), 261.

At the same time a larger volume of oxygen would tend to diffuse into the soil to meet the demand there created. There would, on account of these changes, be a tendency for the percentage of nitrogen to increase in the soil gas, so that its partial pressure would rise above that in the atmosphere, and thus cause nitrogen to diffuse outwards. The same would apply to the argon, but the quantities of this element taking part in the gaseous interchanges are too small to affect our principal conclusions and have been neglected from the calculated quantities. The analyses quoted in Table XIII show also that the above description of the processes is correct ; the proportions of nitrogen and carbon dioxide have risen whilst those of oxygen have fallen in all parts of the soil. The calculation shows that :—

0·429 c. dm. of nitrogen

0·017 c. dm. of carbon dioxide

were diffusing out of the soil, whilst,

0·454 c. dm. of oxygen was diffusing into the soil per day, when the samples were taken.

The question then follows, how do these quantities compare with those involved in the laboratory experiments made in closed vessels ? Assuming that the production of carbon dioxide commenced principally after the heavy rain of June 9th, and remained substantially constant, 0·17 c. dm. or 170 c. c. CO_2 per sq. dm. passed out of the surface soil during the 10 days, and since we know that the nitrate was formed in the second 6″ of soil, and that a good deal of CO_2 was formed in this stratum, the total amount must be distributed throughout this depth. The depth is equivalent to approximately 3 dm., and the weight of dry soil in 3 c. dm. is about 4,000 grams. Thus the quantity of carbon dioxide formed in 10 days in the soil is equivalent to $\frac{170}{40}$ = 4·2 c.c. per 100 grm. soil. It is also necessary to refer to the carbon dioxide which was present as calcium bicarbonate. Although its amount, at any one time, exceeds that which is in the gaseous state, this solution is comparatively stationary in the soil, and calculation shows that its quantity is so much less than that estimated to have diffused out of the soil during 10 days that it may be neglected from the estimate. In the experiment with 100 grams of soil enclosed in the bottle, 31 c.c. (approximately) were formed during 22 days. If more oxygen had been present more carbon dioxide *might* have been formed, and conversely the carbon dioxide which was formed may have been largely formed in the earlier part of the period. However the comparison is made, the quantity of this gas which is calculated to have diffused from the soil seems to be distinctly smaller than the laboratory experiment would indicate. On the other hand considering that the soils were not

identical—though of the same class—that more carbon dioxide may have been diffusing from the field in the earlier days, *i.e.*, before the samples were taken and the conditions in other respects very different, a close agreement could not be expected.

Turning to the oxygen, the volume which is calculated to have been diffusing is obviously far in excess of the volume of carbon dioxide, and is indeed very large. The laboratory experiment with 100 grams of soil in the closed vessel showed that not only about 52 c.c. of oxygen disappeared when 31 c.c. of CO_2 was produced, but that nearly all the oxygen was assimilated in one way or another. The quantity of oxygen calculated to be diffusing, 0·454 c. dm. per day, is equivalent to $\frac{4·54}{40}$ = 0·131 c. dm. per 100 grams of soil in 10 days, assuming that it was all required by the first 3 dm. (about 12″) of soil. There is however reason to suppose that some oxygen is constantly diffusing into the sub-soil.

The next case for consideration is that of the green-manured soil of 1914 (Table VIII). The calculation yields the following quantities :—

Date	14-9-14	17-9-14	20-9-14
Porosity	0·215	0·107	0·159
Gas	C. dm. per sq. dm. per day.		
N	0·7591	0·2082	0·4751
CO_2	0·1436	0·0023	0·0502
	0·9027	0·2105	0·5253
O	0·9619	0·2175	0·5457

Here, again, the process involves a diffusion of nitrogen and carbon dioxide from the soil into the atmosphere, and a diffusion of oxygen into the soil. The oxygen is largely in excess of the carbon dioxide. The quantities found to be diffusing at succeeding times varied greatly, which was to be anticipated from the rainfall conditions. Only light rain fell during the first three days after digging in the san hemp ; heavy rain fell on the evening of 16th, thus

reducing the porosity of the soil very seriously: no further rain fell, and the porosity of the soil naturally increased again before June 20th, thus allowing increased quantities of gas to diffuse. In this instance all that one can do is to compare the calculated quantities of carbon dioxide with the amount of carbon in the san hemp. The san hemp was equivalent to 6·13 gram of dry plant per sq. dm. of soil surface, containing approximately 3·37 gram of carbon. The mean of the three quantities of carbon dioxide estimated to have been diffusing is 0·0658 c. dm. per day which is equal to 0·1295 grm. carbon dioxide or 0·0353 grm. carbon. Thus assuming a *uniform* oxidation of the san hemp, this would be complete in $\frac{3\cdot37}{0\cdot0353} = 95$ days.

It is well known that the leaf and more delicate parts of a green plant which is mixed with damp soil disappear—in India—very rapidly, but that the wood—cellulose and lignin—remain for much longer. Thus the rate of carbon dioxide formation which has been deduced from the rate of diffusion is quite in accord with what might be anticipated from a general knowledge of the subject, and provides an indirect check on the value of the porosity factor as deduced by Buckingham. The quantity of oxygen diffusing is again much in excess of that required for the carbon dioxide. Regarding the quantities of oxygen which are thus calculated to be diffusing, it must be realized that if they are too high, this could only be due to incorrectness of Buckingham's factor, and any alteration of this would affect all the gases equally. If then it is fair to conclude that the calculated amounts of carbon dioxide are what might be expected under the circumstances, those calculated for oxygen must be similarly admitted as near the truth. It is also to be recollected that the oxygen assimilated has been debited entirely to the upper soil, whereas the sub-soil may be, and probably is, absorbing oxygen also. The cause of this absorption (apart from CO_2 formation) is unknown, but it evidently exists.

The third set of quantities of diffusing gases which may be considered are those of the soil in the neighbourhood of growing crops. The gas analyses are set out in Table X. Here nitrogen, carbon dioxide and in some cases hydrogen were passing out of the soil, whilst oxygen diffused into it. The calculated quantities are set out in the accompanying Table XVI.

Here we have no extraneous evidence with which to compare these quantities. They vary on different dates in part according to the rainfall, and in part reflect the activities of the plant at different times. Large quantities of carbon dioxide are constantly produced and much larger quantities of oxygen are constantly absorbed, and these are similar in magnitude to those accom-

Table XVI.

Volumes of gases diffusing from and into the soil near the roots of growing crops.

San Hemp.

Date	27-7-14	30-7-14	3-8-14
Porosity	0·250	0·1954	0·1493
	C. dm per sq. dm. per day		
N	1·3750	0·5079	0·1373
CO_2	0·3908	0·0301	0·0016
	1·7658	0·5380	0·1389
O	1·9060	0·5546	0·1413

Indigo.

Date	18-8-14	20-8-14	23-8-14
Porosity	0·135	0·212	0·1774
	C. dm. per sq. dm. per day		
N	0·4193	0·4425	0·2556
CO_2	0·0212	0·1680	0·0191
H	....	0·1236	0·0523
	0·4405	0·7341	0·3270
O	0·4502	0·7016	0·2982

Maize.

Date	6-9-14	8-9-14	10-9-14
Porosity	0·1465	0·194	0·159
	C. dm. per sq. dm. per day		
N	0·2552	0·1675	0·4872
CO_2	0·0083	0·0244	0·0324
H	0·1164	0·1144	.. ..
	0·3799	0·3063	0·5196
O	0·3010	0·2331	0·5342

panying a recent application of green manure. In some cases they are larger. The quantity of hydrogen is notable.

There is one fact in relation to this subject that deserves very special consideration. The quantities of gas diffusing from or into the soil in the neighbourhood of growing crops, even in very wet weather, are quite as great as where a green manure had been recently dug in : they are also as great as, or greater than, where the fallow soil had become wetted by the early monsoon rainfall, and they are greater than the volumes which were diffusing through the fallow soil previous to the monsoon rainfall. In what respect then does the cultivation of the surface soil affect gaseous interchange ? Naturally if land is disturbed by the plough or harrow, the gases in that particular stratum of soil have a much greater facility for diffusion than if the soil were not disturbed, but there is nothing to show that this operation affects the gases in the several feet of soil below it. Even supposing Buckingham's factor to be largely in error, the above argument would not be impaired, for whatever the actual quantities diffusing, the fact remains that the process goes on quite freely through the soil when thoroughly wet by the monsoon or at least sufficiently so for all needs of plant life. Although the proportion of oxygen was so small in the neighbourhood of the roots of the several crops, these were not only healthy but were indeed very fine ones. The value of good cultivation is of course an established fact, but that one of its chief advantages lies in a more perfect aeration of the soil is extremely doubtful.

Conclusion.

The information collected by the examination of soil gases has provided more precise information than has hitherto been obtained, principally on the following points :—

(*i*) The volume of gas in soils under different moisture conditions has been obtained by *direct measurement* as distinct from that derived from the volumes of siliceous matter and water, and assuming the difference figures to be equal to the gas volume. The volume obtained by direct measurement has been found approximately equal to that obtained by the indirect calculation.

(*ii*) The volume of condensed gas in the Pusa soil is so small that it cannot be estimated with accuracy and is certainly not greater than 4% of the total gas present.

(*iii*) The volumes of gas during wet weather are naturally smaller than when the soil is dry because as water enters a soil, it displaces

some of the gas. The volume of displaced gas is not necessarily equal to the additional water, and the experimental results also show that 1 volume of water does not necessarily displace 1 volume of gas. At the same time the two approach equality.

(*iv*) The whole of the gas is not displaced from a soil; indeed even during the wettest weather the proportionate volume of gas only falls to 15 or 20% or about one half the volume which is present during long periods of hot dry weather.

(*v*) The soil gas of land which has been freshly treated with farm manure or green manure naturally contains a high proportion of carbon dioxide and a low proportion of oxygen, but it is evident from the information gained by operating with closed vessels (containing abundance of air) that were it not for the process of diffusion, the proportions would be very different from what they are.

(*vi*) One of the most striking items of information which the investigation has provided is the composition of the gases in the neighbourhood of the roots of plants. Carbon dioxide has been known to be a constant accompaniment of plant growth, but whilst no definite numerical statements have been hitherto possible, the proportions which have been actually found must be considered high. More striking however is the low proportion of oxygen, and the presence of hydrogen has not hitherto been suspected under these conditions.

It is generally held that carbon dioxide is a product of the higher plant, but there is no experimental proof that this compound, although constantly present in the neighbourhood of the roots of crops, is not produced actually by lower organisms. Moreover the liberation of hydrogen gas must be due to the agency of an entirely different class of bio-chemical change from that concerned with the assimilation of oxygen or the production of carbon dioxide.

In the Memoir on Drainage (p. 97) I took the opportunity of calling attention to the very limited information in our possession regarding the associations of our crops with lower organisms, and the composition of the gases in the neighbourhood of crop-roots likewise emphasizes the importance of this subject.

(*vii*) Although high proportions of carbon dioxide are frequently present in the gas as extracted from the soil, calculation shows that considerably the greater part is present in the dissolved state in the soil solution. We are ignorant of the relative physiological significance of the two states of this compound, but it is at least certain that from the chemical standpoint, the dissolved portion would be the active agent in any series of changes.

(*viii*) It is quite easy to determine the O/A or N/A ratio in small amounts of soil gas within about 1/10 of the true value. The determination of these ratios although open to this error, has shown with great certainty that the chief changes in the soil have to do with the oxygen, whilst nitrogen-assimilation or nitrogen-evolution in dry land is at least so limited that it is usually difficult to detect.

On the other hand, in cases like the gas from rice land, the argon determination demonstrates with certainty that most of the nitrogen is derived from the soil and manure.

(*ix*) The amounts of the gases diffusing into or out of the soil have been calculated for a number of instances on the assumption that Buckingham's estimate of the effect of soil porosity is substantially correct. The result of these calculations is to show that the carbon dioxide diffusing out of the soil is much about what one would anticipate from independent evidence. At the same time very large amounts of oxygen pass into the soil, these being greater than might be expected from the amounts of carbon dioxide or nitrate which may be found concurrently. It is difficult to suggest a really satisfactory explanation for the utilization of such large amounts of this element.

(*x*) Whether the correctness of these calculated amounts of diffusing gases be allowed or not, it is certain that diffusion of gases through soils at a depth of 12—15″ is so efficient as to warrant the conclusion that cultivation of the surface soil is unnecessary for purposes of aeration. The well-established value of good cultivation must be referred to other causes.

PUSA,
May 4th, 1915.